

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-048801

(43)Date of publication of application : 20.02.1996

(51)Int.Cl.

C08J 7/04
B05D 7/02
B05D 7/24
C09D175/04

(21)Application number : 06-184997

(71)Applicant : TOYODA GOSEI CO LTD

(22)Date of filing : 05.08.1994

(72)Inventor : WATARAI HIROSHI

TAKADA RYOICHI

SEKIYA TAKASHI

MIYAJIMA YASUHIRO

(54) COATED POLYOLEFIN MOLDED ARTICLE

(57)Abstract:

PURPOSE: To obtain a coated polyolefin molded article comprising a top coating film which is primerless for a PO molded article and has sufficient coating film adhesivity and coating performance dealing with exterior automotive trim in terms of gasoline resistance and luster.

CONSTITUTION: This coated polyolefin molded article is obtained by forming a top coating film on a PO molded article without through an under coating film. The top coating film is composed of a baking type urethane-based coating compound comprising a mixture, as a polyol component, of (1) a hydroxy prepolymer obtained by grafting an acrylic acid glycol ester onto a chlorinated PO, urethanizing the graft polymer with an organic diisocyanate and a polymer polyol and further grafting an α -olefinic monomer onto the urethanized polymer and (2) an acrylic polyol containing styrene, an acrylic acid lower alkyl ester, an acrylic acid alkylene glycol ester and an acrylic acid polyalkylene glycol ester as essential polymerization units.

* NOTICES *

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]It is the paint polyolefin molding in which a finish coating film is formed on polyolefine (PO) mold goods without passing an under coat coat, A paint polyolefin molding, wherein said finish coating film is formed in burned type urethane system paints which use a mixture of following acrylic urethane denaturation chlorination PO** and following specific acrylic polyol ** as a polyol ingredient.

** A hydroxy prepolymer to which the hydroxy prepolymer was made to form by organic diisocyanate and polymer polyol (urethane-izing), and the graft polymerization of the alpha olefin nature monomer was further carried out after carrying out the graft polymerization of the acrylic acid (meta) glycol ester to the chlorination PO.

** Acrylic polyol which contains styrene, acrylic acid (meta) lower alkyl ester, acrylic acid (meta) alkylene glycol ester, and acrylic acid (meta) polyalkylene glycol ester as a polymerization indispensable unit.

[Claim 2]A paint polyolefin molding characterized by the mixture ratio (weight ratio) of acrylic urethane denaturation chlorination PO** and following specific acrylic polyol ** being **/=95 / 5 - 15/85 in claim 1.

[Claim 3]In claim 1, said specific acrylic polyol as a polymerization indispensable unit Styrene, A paint polyolefin molding being what contains methacrylic acid butylester, methacrylic acid ethylene glycol ester, and methacrylic acid poly(n= 6-10) tetramethylen glycol ester as indispensable.

[Claim 4]In claim 3, said specific acrylic polyol as a polymerization indispensable unit 15-25 mol of styrene %, A paint polyolefin molding being a thing containing 5-15 mol of 15-25 mol of 40-60 mol of methacrylic acid butylester % and methacrylic acid ethylene-glycol-ester % and methacrylic acid poly(n= 6-10) tetramethylen glycol ester %.

[Translation done.]

* NOTICES *

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the new paint polyolefin molding in which the finish coating film is formed on PO mold goods without passing an under coat coat. Here, as a polyolefin molding, exterior parts for cars, such as a bumper, a side mall, and SAIGANISSHU, can be mentioned.

[0002]Here, although PP mold goods are taken and explained to an example as PO mold goods, it is not restricted to this.

[0003]Hereafter, the following of the main thing of the cable address of the polymer used on these specifications is carried out.

[0004]PO -- Polyolefine PP -- Polypropylene, chlorination PO -- Chlorinated polyolefins [0005]

[Description of the Prior Art]A polyolefin system plastic, especially PP are excellent in chemical resistance, a water resisting property, a moldability, etc., and since it is cheap still lighter-weight, they are used abundantly at autoparts, such as a bumper, a side mall, and side garnish. However, since PP is inferior to abrasion-proof nature and weatherability, with mold goods, it is rare to be able to use it as a product, and it needs to paint in paints baking (heat curing) type [, such as a urethane resin system paint,] for surface treatment to serve also as an ornament.

[0006]However, since PP is nonpolar material, the above polar resin system paints do not adhere at all.

[0007]For this reason, for example, the finish coating film was given after steam cleaning (it mainly aims at surface surface roughening) by 1,1,1-trichloroethane (TCE) after applying the top coat which has a reaction adhesive property with a finish coating film (references, such as JP,3-22895,B).

[0008]

[Problem(s) to be Solved by the Invention]However, TCE has a problem of environmental pollution and it will become impossible to use it in the future (1995 abolition). On the other hand, if TCE washing is not performed to a substrate (mold goods), it is difficult to get to a raw material in sufficient film adhesion.

[0009]It has been requested that a finish coating film is directly formed from the standpoint of the productivity of paint mold goods these days, without passing primer loess, i.e., an under coat coat.

[0010]Then, the constituent for "covering of the following composition is proposed in JP,5-263038,A.

[0011]"After carrying out the graft copolymerization of the monomer which carries out the piece owner of the hydroxyl group to an ethylene nature unsaturated bond at least into one molecule to chlorinated polyolefins, It urethane-izes by organic JIISOSOANETO and polymer polyol, Constituent for covering

produced by carrying out the graft copolymerization of the monomer containing at least one hydroxyl group to an ethylene nature unsaturated bond in the monomer which contains at least one ethylene nature unsaturated bond in one more molecule, and/or one molecule. Only " is carried out, In [when a coat is formed on PO mold goods with the burned type urethane system paint which uses the above-mentioned constituent as a polyol ingredient, as a result of this invention persons' doing test examination] urethane film properties especially gasoline-proof nature, and glossiness, When it applied to automobile exterior parts, such as a bumper, it turned out that it is insufficient.

[0012] This invention is primer loess even if a finish coating film does not pass through the process of TCE washing to PO mold goods in view of the above, While having sufficient film adhesion, it is in providing the paint polyolefin molding which has the coat performance which can respond to automobile exterior parts also in gasoline-proof nature, gloss, etc.

[0013]

[Means for Solving the Problem] This invention solves an aforementioned problem by the following composition.

[0014] It is the paint polyolefin molding in which a finish coating film is formed on PO system mold goods without passing an under coat coat, A paint polyolefin molding, wherein a finish coating film is formed in burned type urethane system paints which use a mixture of following acrylic urethane denaturation chlorination PO** and following specific acrylic polyol ** as a polyol ingredient.

[0015]** A hydroxy prepolymer to which the hydroxy prepolymer was made to form by organic diisocyanate and polymer polyol (urethane-izing), and the graft polymerization of the alpha olefin nature monomer was further carried out after carrying out the graft polymerization of the acrylic acid (meta) glycol ester to the chlorination PO.

[0016]** Acrylic polyol which contains styrene, acrylic acid (meta) lower alkyl ester, acrylic acid (meta) alkylene glycol ester, and acrylic acid (meta) polyalkylene glycol ester as a polymerization indispensable unit.

[0017]

[Detailed Description of the Means for Solving the Problem] Hereafter, each means of this invention is explained in detail. By the following explanation, unless it refuses, let especially a combination unit be a gravitational unit.

[0018] A. Let the paint polyolefin moldings in which the finish coating film is formed on PO mold goods without passing an under coat coat be the requirements for a premise.

[0019] As PO mold goods, the mold goods which consist of PO system thermoplastic elastomer and a styrene thermoplastic elastomer are contained here besides PP system mold goods which consist of crystalline PP, a PP copolymer, entering rubber PP, etc.

[0020] B. As for the paint polyolefin molding of this invention, a finish coating film is (1). The acrylic urethane denaturation chlorination PO and following (2) It is formed in the burned type urethane system paints which use a mixture with specific acrylic polyol as a polyol ingredient.

[0021] (1) In the above-mentioned acrylic urethane denaturation chlorination PO. After carrying out the graft polymerization of the acrylic acid (meta) glycol ester to the chlorination PO, By the thing of the hydroxy prepolymer to which the hydroxy prepolymer was made to form by organic diisocyanate and polymer polyol (urethane-izing), and the graft polymerization of the alpha olefin nature monomer was carried out further.

Usually, what satisfies the following requirements among "the constituents for covering" indicated to said JP,5-263038,A is used.

[0022]** Chlorination PO content is 20 to 80%. At less than 20%, if it is inferior to the adhesion over PO mold goods and 80% is exceeded, the balance of film properties will worsen.

[0023]** Weight average molecular weight is 2000-100000. In less than 2000, difficult to get, if 100,000 is exceeded, coat viscosity will be too high and a problem will become easy to generate the coat which has sufficient intensity to handling nature.

[0024]** A glass transition point (Tg) is -30-80 **. -In less than 30 **, if a coat tends to present adhesiveness (tuck nature) and exceeds 80 **, a coat will become weak and it will be easy to generate a crack.

[0025]** Hydroxyl values (OH value) are 30-150. In less than 30, if the crosslinking density of a cured film is low, it becomes easy to generate a problem in solvent resistance and 150 is exceeded, it will become easy to generate a problem in the film adhesion over a substrate.

[0026]** Chlorine content is 5 to 40%. In less than 5%, film strength is difficult to get, and if 40% is exceeded, it will become easy to generate a problem in the film adhesion over a substrate.

[0027]As the above-mentioned (meta) acrylic acid glycol ester, Those derivatives (what was esterified by KAPURORAKUTAN), such as 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, and 2-hydroxybutyl (meta) acrylate, can be mentioned.

[0028]As the above-mentioned organic diisocyanate, although aromatic series, aliphatic series and alicycle fellows, and any may be sufficient, when applying to automobile exterior equipment, the non-**** type of the following aliphatic series thru/or alicycle fellows is desirable.

[0029]1,4-tetramethylene di-isocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-hexamethylene-di-isocyanate, isophorone diisocyanate, 4, and 4-dicyclohexylmethane diisocyanate, 1, 4-cyclohexyl diisocyanate, etc.

[0030]As the above-mentioned polymer polyol, it is usable in general-purpose polyether polyol (polymer of glycol, etc.), and polyester polyol (dicarboxylic acid and resultant of glycol).

[0031]As the above-mentioned alpha olefin nature monomer, acrylic acid (meta), acrylate (methacrylate), acrylic acid glycol ester, hydroxy acrylate, styrene, vinyl acetate, etc. can be mentioned.

[0032](2) specific acrylic polyol is a thing containing styrene, acrylic acid (meta-) lower alkyl ester, acrylic acid (meta-) alkylene glycol ester, and acrylic acid (meta-) polyalkylene glycol ester as a polymerization indispensable unit.

[0033]Styrene bears here the operation which gives hardness to a coat, and acrylic acid (meta) lower alkyl ester, Bearing the operation which gives softness to a coat, acrylic acid (meta) alkylene glycol ester and (meta) acrylic acid polyalkylene glycol ester bear the operation which reacts to an isocyanate and stiffens a coat. And acrylic acid (meta) polyalkylene glycol ester does so the operation where the distance between the points constructing a bridge lengthens, which raises the toughness (abrasion-proof nature) and weatherability of a coat by existence of polyalkylene further and which both increases miscibility with the acrylic modification P0.

[0034]In order to make each above-mentioned operation bear certainly, it is desirable that it is what contains styrene, methacrylic acid butylester, methacrylic acid ethylene glycol ester, and methacrylic acid poly(n= 6-10) tetramethylen glycol ester as indispensable as a polymerization indispensable unit.

[0035]As a polymerization indispensable unit, more specifically 15-25 mol of styrene %, Suppose that it is a thing containing 5-15 mol of 15-25 mol of 40-60 mol of methacrylic acid butylester % and methacrylic acid ethylene-glycol-ester % and methacrylic acid poly(n= 6-10) tetramethylen glycol ester %.

[0036]This specific acrylic polyol usually uses what satisfies the following requirements.

[0037]** Weight average molecular weight is 3000-50000. In less than 3000, difficult to get, if 50000 is exceeded, coat viscosity will be too high and a problem will become easy to generate the coat which has sufficient intensity to handling nature.

[0038]** A glass transition point (Tg) is -30-80 **. -In less than 30 **, if a coat tends to present adhesiveness (tuck nature) and exceeds 80 **, a coat will become weak and it will be easy to generate a crack.

[0039]** Hydroxyl values (OH value) are 30-150. In less than 30, if the crosslinking density of a cured film is low, it becomes easy to generate a problem in solvent resistance and 150 is exceeded, it will become easy to generate a problem in the film adhesion over a substrate.

[0040](3) The mixture ratio (weight ratio) of the above-mentioned acrylic urethane denaturation chlorination PO** and specific acrylic polyol ** sets to **/=95 / 5 - 15/85. It becomes easy to generate a problem in adhesion-proof here as the coat which has the gasoline-proof nature and the gloss which can respond to automobile exterior parts as too little [specific acrylic polyol] being difficult to get, and specific acrylic polyol being superfluous.

[0041]They carry out addition mixing of the subsidiary materials, such as a solvent and also paints, and the above-mentioned acrylic urethane denaturation chlorination PO and specific acrylic polyol consider it as a polyol ingredient, add organic polyisocyanate just before spreading, and prepare the urethane paint of viscosity suitably while they consider it as the mixture ratio suitably.

[0042]As a solvent, an aliphatic hydrocarbon system, an ester system, an alicycle fellows hydrocarbon system, a ketone system, an aromatic hydrocarbon system, an alcoholic ether system, etc. can be used here.

[0043](4) in this way, the finish coating as the former after applying to PP mold goods with prepared same top coat -- the same -- after spreading -- baking (for example, 80 **x 30 minutes) -- carry out. The film thickness of the top coat at this time may usually be 10-50 micrometers.

[0044]

[Function and Effect of the Invention]In the paint polyolefin molding in which the paint polyolefin molding of this invention is baked, without passing an under coat coat on PO mold goods like the above, and form topcoat is formed, By forming the finish coating film in the burned type urethane system paints which use the mixture of the specific acrylic urethane denaturation chlorination PO and specific acrylic polyol as a polyol ingredient, As the below-mentioned example of an examination shows, the finish coating film of a paint polyolefin molding has the coat performance which can respond to automobile exterior parts also in gasoline-proof nature, gloss, etc. even if it does not pass through the process of TCE washing to PO mold goods, and while having film adhesion sufficient by primer loess.

[0045]

[Test Example(s)]Hereafter, the example and comparative example which checks the effect of this invention and which was performed for accumulating are explained.

[0046](1) The solid content specification of the acrylic urethane denaturation chlorination PO (40% toluene

solution) and specific acrylic polyol (toluene / xylene 50% solution) used by this invention is as follows, respectively.

[0047]Acrylic urethane denaturation chlorination PO chlorine content : 12**1%, melting point:60 **, Weight average molecular weight : 55000, Tg:10 **, chlorination PO content:45%, OH value: -- 66 specific acrylic polyol polymer presentation: -- styrene 19mol%. Methacrylic acid butylester 50mol%, methacrylic acid ethylene-glycol-ester 22mol%, methacrylic acid poly(n= 8.1) tetramethylen glycol ester 8mol%OH value: -- 100, weight-average-molecular-weight:8000, and (2) Next, While adding 24 copies of paints (gray: titanium oxide system), and two copies of stabilizer to 100 copies of mixtures of the display ratio of the above-mentioned acrylic urethane denaturation chlorination PO (40% toluene solution) and specific acrylic polyol and preparing a polyol ingredient, To this polyol ingredient, the HMDI system isocyanate component (NCO = 16.5%) was added so that it might become equivalent ratio, and it stirred for 10 to 11 seconds by "Iwata cup NK-II", and each urethane paint was prepared.

[0048](3) And after carrying out spray coating (30-40 micrometers of thickness) of each paint to the bumper made from entering rubber PP (PP substrate) which carried out IPA ****, it burned on the conditions for 80 **x 30 minutes.

[0049](4) In this way, about the obtained specimen, coat system performance testing of the following item was done.

[0050]** Primary adhesion -- Grid friction test after 24-hour room temperature neglect (JISK5400)

** Secondary adhesion -- Grid friction test of ** after 40 ** warm water x240h immersion (JISK5400)

** Gasoline-proof nature -- The specimen was immersed in gasoline and time until abnormalities (separation, blistering, etc.) occur in the appearance of film was measured.

[0051]** Glossiness -- Reflectance was measured by 60-degree specular reflexion.

[0052]** Low-temperature flexibility (-20 **) -- visual observation of the coat after carrying out the 180-degree price of the specimen to a 1-inch mandrel in -20 ** atmosphere -- it carried out.

[0053]** Cold shock nature (-20 **) -- In -20 ** atmosphere, a 500g steel ball was dropped from a height of 50 cm, and visual observation of the state of a coat was carried out.

[0054](5) The table 1 showing a test result shows having adhesion with each top coat of an example good regardless of the existence of pretreatment (TCE washing and IPA). On the other hand, it turns out that the comparative example 1 which does not contain specific acrylic polyol has a problem in gasoline-proof nature and gloss. It turns out that the comparative example 2 with superfluous specific acrylic polyol has a problem in film adhesion.

[0055]

[Table 1]

	比較例 1	実施例 1	実施例 2	実施例 3	比較例 2
アクリルウレタン変性 塩素化P O /アクリル ポリアル混合比	10/0	9/1	5/5	2/8	1/9
1 次 密 着 性	0/100	0/100	0/100	0/100	3/100
2 次 密 着 性	0/100	0/100	0/100	0/100	10/100
耐ガンリン性	4分	6分	8分	9分	10分
光沢性 (%)	85%	88%	90%	90%	90%
低温屈曲性 (-20℃)	異常無し	←	←	←	←
低温衝撃性 (-20℃)	異常無し	←	←	←	←

[Translation done.]